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TITLE: HEAT RESISTANT CERAMIC FORMED BODY AND MANUFACTURING METHOD THEREOF

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1. TITLE OF INVENTION

Heat resistant ceramic formed body and manufacturing method thereof.

2. PATENT CLAIMS

[Claim 1]

Heat resistant ceramic formed body which characteristically consists of β-spodumene solid solution or β-eucryptite solid solution comprising of at least one metal selected from the group of magnesium, calcium, zinc, lead, and vanadium, as oxides, at the amount of 0.5 to 7.0 wt%, wherein the average surface coarseness is essentially at most 0.03 μm.

[Claim 2]

Manufacturing method of the heat resistant ceramic formed body <u>having a smooth surface with the average surface coarseness of at most 0.03 μm</u>, wherein glass comprising the oxide composition of 50 to 65 wt% of SiO_2, 18 to 30 wt% of Al_2O_3, 3 to 8 wt% of Li_2O, 3 to 5 wt% of $TiO_2 + ZrO_2$, at most 8 wt% of P_2O_5 and (or) B_2O_3 in total, 0.3 to 7.0 wt% of RO (wherein R is a metal atom selected from the group of magnesium, calcium, zinc, lead, and vanadium), and at most 3.0 wt% of R_2O (wherein R is either potassium atom or sodium atom) is formed into <u>a formed body having the desired shape and smooth surface</u>; the obtained glass formed body is thermally treated at the temperature of at most the deformation temperature of the said glass in order to form crystalline nuclei; and β-spodumene solid solution or β-eucryptite solid solution is characteristically formed by increasing the temperature.

[Claim 3]

Reflection mirror material which characteristically consists of β-spodumene solid solution or β-eucryptite solid solution comprising of at least one oxide of metal selected from the group of magnesium, calcium, zinc, lead, and vanadium at the amount of 0.3 to 7.0 wt%, wherein the average surface coarseness is essentially at most 0.03 μm.

[Claim 4]

Manufacturing method of the heat resistant ceramic formed body having a smooth surface with the average surface coarseness of at most 0.03 μm, wherein glass comprising the oxide composition of 50 to 65 wt% of SiO_2, 18 to 30 wt% of Al_2O_3, 3 to 8 wt% of Li_2O, 3 to 5 wt% of $TiO_2 + ZrO_2$, at most 8 wt% of P_2O_5 and (or) B_2O_3 in total, 0.3 to 7.0 wt% of RO (wherein R is a metal atom selected from the group of magnesium, calcium, zinc, lead, and vanadium), and at most 3.0 wt% of R_2O (wherein R is either potassium atom or sodium atom) is formed into a formed body having the desired shape and smooth surface; the obtained glass formed body is thermally treated at the temperature lower than the deformation temperature of the said glass by 50 to 100 °C in order to form crystalline nuclei; and β-spodumene solid solution or β-eucryptite solid solution is characteristically formed by increasing the temperature.

3. DETAILED EXPLANATION OF INVENTION

[Industrial Application Field]

The present invention relates to the heat resistant ceramic formed body having a good surface smoothness and the manufacturing method thereof. The present invention also relates to the reflection mirror substrate material which has a superior heat resistance and endures the use at high temperature.

[Conventional Techniques]

Light source lamps for illumination devices and projectors have larger heat generation as their brightness increases. Therefore, the temperature increase for the reflection mirror used with lamps is also severe. Particularly, recent lamps used in many fields are much brighter with a smaller size, thus the temperature at the reflection mirror sometimes exceeds 550 °C. The reflection mirror is made of the substrate and the reflection film coated on the surface of the substrate, both of which determine the heat resistance of the reflection mirror. Considering the heat resistance of the substrate, the maximum usage temperature and the heat shock resistance are important. For the glass often used as the substrate, the maximum usage temperature is at most the transition temperature, therefore, even the Pyrex level glass having the highest heat resistance is used at the temperature of at most 550 °C, and the heat shock resistance is limited to the temperature difference of 250 °C based on the solid bar (5 mm diameter) test. Therefore, safe usage is difficult under the said severe condition. In addition, the heat resistance limit of the substrate may limit the compact sizing of lamps and reflection mirrors.

The material with higher heat resistance is quartz glass, which is a hard material to be formed and processed and difficult for mass-production, leading to a high cost. In general, ceramics are superior in heat resistance, however, it is difficult to form the high precision curvature necessary for the manufacturing of the reflection mirror. Also due to the problem in the surface smoothness, the reflection mirror made of the ceramics has not been practically utilized. Ceramics

(so-called crystallized glasses) which are obtained by the precipitation of β-spodumene solid solution (Li_2O - Al_2O_3 - 4 SiO_2) or β-eucryptite solid solution (Li_2O - Al_2O_3 - 2 SiO_2) in the low expansion glass having the basic three components of Li_2O, Al_2O_3, and SiO_2 through the thermal processing, have a superior heat resistance and allow the polishing necessary for the reflection mirror substrate to be easily carried out at the stage prior to the crystallization. Therefore, they are desirable materials for the reflection mirror. However, no matter how smooth the finish is at the glass stage, the surface becomes coarse during crystallization, which is a disadvantage as the reflection mirror substrate. In other words, a multi-layer reflection film coated on the reflection mirror substrate by vacuum deposition is thin, about 2 μm, therefore, a poor smoothness on the substrate surface causes a not-so-smooth reflection film, which fails to obtain a reflection film with a high reflectivity. The surface coarseness of the conventional crystallized glass was about 0.1 μm, sometime over 0.5 μm, which was not suitable as the substrate for a high reflectivity reflection mirror (the average coarseness of the polished reflection surface for the Pyrex glass type reflection mirror substrate is usually 0.001 to 0.003 μm. Herein, the "average coarseness" refers to the "center line average coarseness Ra" in JIS B0601).

[Problems Solved by Invention]

The purpose of the present invention is to improve the surface smoothness of the crystallized glass product, which has advantageous characteristics as the reflection mirror substrate but has not been utilized as the high reflectivity reflection mirror substrate due to the insufficient surface smoothness. Another purpose of the present invention is to offer the crystallized glass type heat resistant ceramic formed body having an essentially smooth and luster surface which is useful for other applications besides the reflection mirror substrate and the manufacturing method thereof.

[Methods to Solve Problems]

The heat resistant ceramic formed body and the reflection mirror made therewith which are successfully offered by the present invention characteristically consist of β-spodumene solid solution or β-eucryptite solid solution comprising of at least one metal selected from the group of magnesium, calcium, zinc, lead, and vanadium, as oxides, at the amount of 0.3 to 7.0 % (in wt%, also the same below) and their average surface coarseness is essentially at most 0.03 μm. Herein, "the average surface coarseness is essentially at most 0.03 μm" indicates that the original surface, without any polishing treatment after the crystallization process of precipitating β-spodumene solid solution or β-eucryptite solid solution, has the average surface coarseness of at most 0.03 μm.

The present invention also offers the manufacturing method of the said heat resistant ceramic formed body, wherein glass comprising the oxide composition of 50 to 65 wt% of SiO_2, 18 to 30 wt% of Al_2O_3, 3 to 8 wt% of Li_2O, 3 to 5 wt% of $TiO_2 + ZrO_2$, at most 8 wt% of P_2O_5 and (or) B_2O_3 in total, 0.3 to 7.0

wt% of RO (wherein R is a metal atom selected from the group of magnesium, calcium, zinc, lead, and vanadium), and at most 3.0 wt% of R_2O (wherein R is either potassium atom or sodium atom) is formed into a formed body having the desired shape and smooth surface; the obtained glass formed body is thermally treated at the temperature of at most the deformation temperature of the said glass in order to form crystalline nuclei; and β-spodumene solid solution or β-eucryptite solid solution is characteristically formed by increasing the temperature. Herein the glass deformation temperature is the temperature at which the sample bar (a cylindrical bar with 5 mm in a diameter and 30 mm in length) starts to bend when this sample bar is vertically supported with a 5 g load at the top and the temperature is increased at the rate of 5 °C/minute.

[Action]

The ceramics formed body of the present invention consisting of β-spodumene solid solution or β-eucryptite solid solution comprising of at least one metal selected from the group of magnesium, calcium, zinc, lead, and vanadium, as oxides at the amount of 0.5 to 7.0 % and having average surface coarseness of essentially at most 0.03 μm, demonstrates a superior heat resistance specific to crystallized glass consisting of β-spodumene solid solution or β-eucryptite solid solution. In addition, the essentially superior surface smoothness enables its use in the field requiring a heat resistance and a high degree surface smoothness such as the reflection mirror substrate, without difficult polish finishing. Below, the present invention is described in details by interpreting the manufacturing process of the said ceramic formed body.

Raw material minerals necessary to obtain the glass comprising: 50 to 65 wt% of SiO_2, 18 to 30 wt% of Al_2O_3, 3 to 8 wt% of Li_2O, 3 to 5 wt% of TiO_2 + ZrO_2, at most 8 wt% of P_2O_5 and (or) B_2O_3 in total, 0.3 to 7.0 wt% of RO (wherein R is a metal atom selected from the group of magnesium, calcium, zinc, lead, and vanadium), and at most 3.0 wt% of R_2O (wherein R is either potassium atom or sodium atom) are prepared. They are crushed, mixed, heated, and homogenized in the molten condition for glass making, by following the normal glass manufacturing method. The first characteristic of the said glass composition is a slightly lower melting temperature compared to this type of the conventional glass. Therefore, the melting for glassification can be carried out, at most, at 1500 °C. The ratio of RO component has a significant meaning for obtaining the product with a good surface smoothness. The crystallized glass with a good surface smoothness which can be a substrate for the high reflectivity reflection mirror is possibly manufactured only by blending an adequate amount of RO component and by proceeding crystallization at a slightly lower temperature as described later. The components particularly desirable as RO are PbO and VO.

The ratio of other components are also limited to the said region in order to achieve the goals of the present invention. When the SiO_2 component is less than 50%, the glass tends to devitrify during the forming and more than 65% causes melting difficulty. Less than 17% of Al_2O_3 increases the thermal

expansion coefficient and impairs the heat shock resistance and more than 30% causes melting difficulty. Less than 3% of Li_2O causes melting difficulty and more than 8% increases the thermal expansion coefficient. TiO_2 and ZrO_2 are added as nucleation agents and their total of less than 3% takes too long for crystallization and more than 5% causes melting difficulty and devitrification during forming. Other components, P_2O_5, B_2O_3, and R_2O are effective for the improvement of meltability and workability, however, a large amount leads to undesirable results such as devitrification and deformation of the glass formed body. Therefore, the addition of the excess amount should be avoided. The amount for the addition of each P_2O_5 or B_2O_3 is desirably not to exceed 5%.

The obtained glass is formed into a desired shape by the arbitrary methods such as a blow method, press method, roll method, and cast method, as usual for the ordinal glass. Then the section at which the forming precision and surface smoothness are important, for example a reflection film coating surface of the reflection mirror substrate, is finished by polishing as necessary. Then, the glass formed body is placed within a heating furnace and the two step heat treatment for crystallization is carried out. The first heat treatment process is the crystal nucleus forming process in order to precipitate β-spodumene or β-eucryptite fine crystallites uniformly. Uniform creation of fine crystallites by two separate heat treatment processes is commonly employed for the conventional crystallized glass manufacturing method. However, in the conventional manufacturing method, the first heat treatment is usually carried out at high temperature of 750 to 800 °C, by focusing on the progress in the crystal nucleus forming. In contrary, the present manufacturing method of the present invention employs the treatment temperature lower than the deformation temperature of the said glass composition (about 450 to 650 °C for the standard composition), more desirably the temperature lower than the deformation temperature by 50 to 100 °C. Therefore, the first heat treatment temperature does not exceed 650 °C. This temperature condition is important for the final crystallized glass surface to have a smooth and luster surface. The reason is not clear, however, the high treatment temperature results in the coarse surface even with the formed body of the said glass composition.

After creating crystal nuclei by being maintained at the said temperature for 30 minutes to 2 hours, the temperature is raised to 650 to 850 °C, more desirably 700 to 800 °C, and maintained there for 30 minutes to several hours. First β-eucryptite solid solution, then β-spodumene solid solution are formed. The β-spodumene solid solution has a slightly higher thermal expansion coefficient and superior strength than the β-eucryptite. In the conventional crystallized glass, formation of β-spodumene solid solution required a high temperature heat treatment of about 900 to 1200 °C at the crystallization process. For the said glass composition of the present invention, the highest heat treatment temperature is 800 °C, which consumes much less heat energy.

With the β-spodumene solid solution, the obtained crystallized glass is completely devitrified as the crystallization proceeds, however, the surface roughness caused by this is suppressed to the minimum. The average coarseness is at most 0.03 μm. The reflection mirror prepared with the crystallized glass substrate of which average surface roughness is 0.02 μ demonstrates the reflectivity of at least 90% of that similarly prepared with the heat resistant glass substrate of which average surface roughness is at most 0.002. Therefore, it is sufficiently applicable as the reflection mirror substrate. The softening and deformation temperature of the product with the β-spodumene solid solution is at least 900 °C and endures the continuous usage at the temperature up to 700 °C. It also has a superior heat shock resistance and did not break by the test of dropping the object heated to 600 °C into cold water.

[Examples]

Example 1

The raw material was prepared at the following composition: 60% of SiO_2, 21% of Al_2O_3, 5.5% of Li_2O, 4% of TiO_2 + ZrO_2, 5% of P_2O_5, 2.5% of B_2O_3, 4% of ZnO + MgO, and 1.5% of K_2O + Na_2O. Glass was made by melting at 1500 °C and formed into the reflection mirror substrate shape of 80 mm diameter by the press forming method. This glass formed body with the deformation temperature of 660 °C was maintained at 570 °C for 1 hour and the temperature was raised to 770 °C at the temperature increasing rate of 3 °C/min. After maintaining this temperature for 1 hour, the substrate was cooled. The transparent formed body prior to the heat treatment turned milky white and the X-ray diffraction diagram confirmed the β-spodumene solid solution. The thermal expansion coefficient (average value from room temperature to 400 °C) was 6 x 10^{-7} /°C and the bending strength was 900 kgf/cm^2. In addition, dropping into cold water after being heated to 600 °C did not break the product, which confirmed the superior heat shock resistance. The surface had beautiful luster with the average coarseness of at most 0.03 μm. An alternative multi-layer film of Ta_2O-SiO_2 was vapor-deposited on the designed position of the product, and the reflectivity of the obtained reflection mirror was at least 90 over the entire visible region, by assuming the reflectivity of 100 for the reflection mirror made with the said glass reflection mirror substrate without heat treatment but with the same vapor-deposited reflection film.

Example 2

The raw material was prepared at the following composition: 53% of SiO_2, 25% of Al_2O_3, 6% of Li_2O, 4.3% of TiO_2 + ZrO_2, 3% of P_2O_5, 3% of B_2O_3, 3.5% of PbO + MgO, and 1.4% of K_2O + Na_2O. Glass was made by melting at 1470 °C and formed into the reflection mirror substrate shape of 80 mm diameter by the press forming method. This glass formed body with the deformation temperature of 650 °C was maintained at 600 °C for 1 hour and the temperature was raised to 750 °C at the temperature increasing rate of 5 °C/min. After maintaining this temperature for 1 hour, the substrate was cooled. The transparent formed body

prior to the heat treatment turned milky white and the X-ray diffraction diagram confirmed the β-spodumene solid solution. The thermal expansion coefficient was 15×10^{-7} /°C and the bending strength was 950 kgf/cm^2. In addition, dropping into cold water after being heated to 600 °C did not break the product, which confirmed the superior heat shock resistance. The surface had beautiful luster with the average coarseness of at most 0.025 μm. An alternative multi-layer film of Ta_2O-SiO_2 was vapor-deposited on the designed position of the product, and the reflectivity of the obtained reflection mirror was at least 90 over the entire visible region, by assuming the reflectivity of 100 for the reflection mirror made with the said glass reflection mirror substrate without heat treatment but with the same vapor-deposited reflection film.

Comparison Example 1

The raw material the same as in Example 2 except not including PbO and MgO was prepared, i.e., at the following composition: 53% of SiO_2, 25% of Al_2O_3, 6% of Li_2O, 4.3% of TiO_2 + ZrO_2, 3% of P_2O_5, 3% of B_2O_3, and 1.4% of K_2O + Na_2O. Glass was made by melting at 1470 °C and formed into the reflection mirror substrate shape of 80 mm diameter as similarly in Example 2. This glass formed body with the deformation temperature of 650 °C was maintained at 600 °C for 1 hour and the temperature was raised to 750 °C at the temperature increasing rate of 5 °C/min. After maintaining this temperature for 1 hour, the substrate was cooled. The transparent formed body prior to the heat treatment turned milky white and the X-ray diffraction diagram confirmed the β-spodumene solid solution. The product surface coarseness was uneven and the coarse section exceeded the level of 0.3 μm. In addition, the deformation was observed in general. As a result, the reflectivity of the reflection mirror obtained by the vapor-deposition of the multi-layer reflective film as in Example 2 did not reach 90 over the entire visible region, by assuming the reflectivity of 100 for the reflection mirror with the same reflection film vapor-deposited on the polished glass surface.

Comparison Example 2

The glass formed body obtained by the similar method in Example 2 was held at 650 °C for 1 hour and the temperature was raised to 830 °C for an hour heat treatment process. The transparent formed body prior to the heat treatment turned milky white and the X-ray diffraction diagram confirmed the β-spodumene solid solution. Despite a high bending strength of 1400 kgf/cm^2, the thermal expansion coefficient was 20×10^{-7} /°C and the heat shock resistance was at most 500 °C. Further, the average surface coarseness was at least 0.05 μm and wrinkles were observed with the naked eye. As a result, the reflectivity of the reflection mirror obtained by the vapor-deposition of the multi-layer reflective film as in Example 2 was about 80 over the entire visible region, by assuming the reflectivity of 100 for the reflection mirror with the same reflection film vapor-deposited on the polished glass surface.

[Effect of Invention]

As discussed above, the ceramic formed body of the present invention has a superior heat resistance, heat shock resistance, and mechanical strength, and also possesses the extremely smooth luster surface, compared to the conventional crystallized glass. Therefore, they are not only suitable as the reflection mirror substrate, but are also applicable in various fields such as optical materials, electric insulators, and electronic part materials. In addition, according to the present manufacturing method, the product can be offered at lower cost by performing the crystallization at a much lower temperature than the conventional crystallized glass manufacturing process. Further, the product surface has a high degree of smoothness which requires no ordinary polish finishing, therefore, the heat resistant material with a high degree of smoothness can be easily utilized in many fields.